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<p>(21) International Application Number: PCT/US99/12899 (22) International Filing Date: 9 June 1999 (09.06.99) (30) Priority Data: 60/088,777 10 June 1998 (10.06.98) US (71) Applicant (for all designated States except US): US NANOCORP, INC. [US/US]; 20 Washington Avenue, North Haven, CT 06473-2342 (US). (71)(72) Applicants and Inventors: YE, Hui [CN/US]; Apartment 210, 10680 Hampshire Avenue, Bloomington, MN 55438 (US). STROCK, Christopher [US/US]; 76 Wildwood Road, Storrs, CT 06268 (US). XIAO, Tongsan [CN/US]; 50 Hall Hill Road, Willington, CT 06279 (US). STRUTT, Peter, R. [US/US]; 126 Clover Mill Road, Storrs, CT 06268 (US). REISNER, David, E. [US/US]; 100 Oakland Street, Bristol, CT 06010 (US).</p>	<p>(81) Designated States: CN, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>	
<p>(54) Title: THERMAL SPRAYED ELECTRODES</p> <div data-bbox="600 1134 1112 1323" data-label="Image"> </div> <p>(57) Abstract</p> <p>A method for the synthesis of an electrode (1), and the resulting article (1) therefrom, comprising coating an active material feedstock (3) with an additive material suitable for preventing thermal decomposition of said feedstock (3) during thermal spray, thermal spraying the coated feedstock (3) onto a substrate (2) for an electrode, thereby forming a coating on the substrate (2), thereby providing an electrode (1).</p>		

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THERMAL SPRAYED ELECTRODES

Background of the Invention

1. Field of the Invention.

The present invention relates to the manufacture of porous electrodes for energy storage devices and energy conversion devices by chemical and thermal spray techniques. In particular, this invention relates to the fabrication of thin film oxide and non-oxide electrodes by thermal spray. Such manufacture advantageously uses continuous processes suitable for high-volume electrode production.

2. Description of the Related Art

Energy storage devices, such as batteries and supercapacitors, and energy conversion devices, such as fuel cells and thermoelectrics, both require electrodes comprising an active material for the energy storage, conversion, and/or release processes. Each year, billions of dollars are spent on both primary and rechargeable batteries for use in applications ranging from small batteries for portable electronics and communications equipment, to larger batteries used for automobiles and uninterruptible power supplies (UPS). Many of the industrial manufacturing processes associated with the fabrication of the electrodes containing active material (faradaic) are based on batch processes, often incorporating labor-intensive hand

operations. There exists a critical need to develop continuous processes for electrode manufacture that enable the production of low-cost electrodes for both energy storage and energy conversion devices.

There is especially a need for efficient manufacture of thin film electrodes (e.g. 10 mil or less), where conventional pressing techniques are inappropriate for disk electrodes with diameter in excess of 2 inches in the absence of a supporting substrate. Thin film electrodes have been fabricated by various techniques, including spray pyrolysis and chemical vapor deposition (CVD). Spray pyrolysis is used in the preparation of thin films comprising metal oxides. In spray pyrolysis, a negatively-charged substrate with a heating element to control the temperature is provided, and a precursor solution with the proper molar ratio is forced to flow through a positively charged nozzle onto the negatively charged substrate. The spray droplets tend to move to the hot substrate, primarily due to electrostatic attraction, and pyrolysis takes place at or near the surface of the substrate. This technique has been used to fabricate electrodes comprising LiCoO_2 , LiMn_2O_4 , yttria stabilized zirconia (YSZ).

Thin film electrodes have also been previously fabricated by chemical vapor deposition (CVD) and related techniques. A typical CVD process involves the steps of vaporizing precursors to the vacuum chamber; triggering reaction of the vaporized precursors; and depositing the reaction product onto the surface of substrate. This basic process has been used to fabricate electrodes comprising MoS_2 by conventional CVD, $\text{ZrO}_2\text{-TiO}_2\text{-Y}_2\text{O}_3$ by laser CVD (wherein the laser is the heat source of the substrate and reaction activator), and TiS_2 by plasma CVD.

Thin film electrodes have also been prepared by sol-gel methods ($\text{CeO}_2\text{-TiO}_2$ electrodes), electrochemical method (amorphous MnO_2 electrodes), and molecular beam deposition ($\gamma\text{-In}_2\text{Se}_3$). Most, if not all of the above-described processes have been limited to small-scale electrode production, and are further ill-suited to adaptation to a continuous process suitable for low-cost, high volume production.

Recently, fabrication of electrodes by thermal spray has been disclosed by U. S. Pat. No. 5,716,422 to Muffoletto et al., which is incorporated herein by reference. U. S. Pat. No. 5,716,422 teaches the use of a variety of thermal spraying processes for depositing an electrochemically active material onto a substrate, resulting in a thin

film electrode. Suitable spraying techniques include chemical combustion spraying processes, for example powder flame spraying, and electric heating spraying processes, for example plasma spraying. Muffoletto et al.'s preferred electrochemically active materials include metals, metal oxides, mixed metal oxides, metal sulfides and carbonaceous compounds and mixtures thereof. More particularly, the use of copper oxide, cobalt oxide, chromium oxide iron sulfide and iron disulfide is disclosed.

A significant drawback of the thermal spraying processes results from the thermal instability of some of the electrochemically active materials, particularly iron disulfide ("pyrite"). Pyrite is thermally unstable, decomposing to FeS at about 550° C, which is much cooler than the flame temperature of plasmas spray. Although certain well-known techniques can provide lower flame temperature, the oxidized nature of the flame (the flame consists of propylene and oxygen) prevents the possibility of its application in the spraying of pyrite.

There accordingly remains a need for methods for producing electrodes using thermal spraying and certain preferred electrochemically active materials while avoiding thermal decomposition of said electrochemically active materials. Further, there exists a need for a thermal spraying process wherein the electrochemically active materials comprise nanostructured materials.

Summary of the Invention

The above-discussed and other drawbacks and deficiencies of the prior art are overcome or alleviated by the method of the present invention, wherein thermal spray of active material feedstocks is used to fabricate porous electrodes for energy storage devices and energy conversion devices. Active material feedstocks for thermal spray are readily available by chemical synthesis in aqueous solution at low temperature (<90°C). In an advantageous feature of the present invention, the active material feedstocks undergo a reprocessing step whereby they are uniformly coated with sulfur prior to thermal spray. The sulfur coating prevents thermal decomposition of the active materials during the spraying process. Thermal spray methods function with a wide variety of active material feedstocks, and are readily adaptable to continuous

manufacturing processes. In another advantageous feature of the present invention, the active material feedstock comprises nanostructured materials, which after thermal spray results in electrodes having nanostructured active materials.

5 The above-discussed and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description and drawings.

Brief Description of the Drawings

10 The FIGURE is a schematic diagram of a coated electrode 1 wherein a substrate 2 is coated with an active material feedstock 3, in accordance with the present invention.

Detailed Description of the Invention

15 In accordance with the present invention, thermal spray of an active material feedstock is used to fabricate porous electrodes. Active material feedstocks for thermal spray are readily available by chemical synthesis in aqueous solution at low temperature ($<90^{\circ}\text{C}$). The purpose of this invention is to enable low cost production of electrodes, either thick or thin film. This invention applies to the fabrication of electrodes using either conventional or nanostructured materials as a feedstock for thermal spray. In a particularly advantageous feature of the present invention, the active material feedstocks undergo a reprocessing step whereby the materials are coated with one or more additives to suppress thermal decomposition during thermal spraying.

25 Active material feedstocks are selected from the group consisting of metals, metal oxides, mixed metal oxides, metal sulfides, carbonaceous materials and mixtures thereof, for example, nickel hydroxide and manganese dioxide. More preferably, the active material feedstocks are metal sulfides, in particular cobalt disulfide, molybdenum disulfide, and tungsten sulfide (WS_2). An especially preferred active material feedstock is iron disulfide (pyrite). Synthesis of thin films of pyrite has previously been investigated. Muffoletto et al. teaches the use of iron disulfide as
30 an active material feedstock for deposit onto a substrate via thermal spray. G.

Pimenta et al. have produced pyrite using H_2S -reactive iron. Pyrite and pyrite films have also been prepared by chemical vapor transportation, sulfurization of iron oxides, electrodeposition of iron films, argon and reactive sputtering, screen printing processes, and chemical vapor deposition. Conventional and fine pyrite (micron-sized) is also produced in aqueous solution.

Pyrite is thermally unstable, decomposing to FeS at about $550^\circ C$. The flame temperature of plasmaspray is thus much hotter than the decomposition temperature of pyrite. Although HVOF can provide lower flame temperature, the oxidized nature of the flame (the flame consists of propylene and oxygen) prevents the possibility of its application in the spraying of pyrite. Accordingly, appropriate steps must be taken to prevent the thermal decomposition of the pyrite.

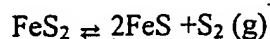
There are at least two ways to suppress the decomposition, the first being to reduce the flame temperature by varying the spray conditions. However, practice has shown that a reduction in flame temperature alone will not fully prevent pyrite decomposition. Consequently, a second method of preventing decomposition may be used in addition to or alternatively to temperature reduction. This second method involves the use of one or more additives to provide a protective coating surrounding the pyrite particles while in the spray gun flame. Preferred additives include cornstarch and sulfur, with sulfur being more preferred.

The coating step comprises mixing a quantity of additive effective to suppress thermal decomposition with the active material feedstock. The composition is mixed using methods known in the art until each component is uniformly dispersed. Ball milling is a particularly effective mixing technique. The composition is then dried if necessary. The surface moisture of the active material feedstock is thereby removed and replaced with a coating comprising the additive. An appropriate additive has relatively high melting and boiling points, accordingly, the coating slows the active material feedstock from heating and prevents thermal decomposition. Additional benefits of the coating include much better flowability of the reprocessed powder and the ability to store the powder outside of a vacuum.

By way of illustration, and in no way intended to be limiting, an exemplary additive material for the purpose of providing a protective coating is elemental sulfur

powder. Sulfur has a melting point of 120°C and boiling point of 440°C, both of which are below the decomposition temperature of pyrite. The aforementioned reprocessing steps provide a sulfur coating on the surface of pyrite particles. As sulfur is a poor heat conductor, the coating slows the heating of the pyrite powder. The coating consumes large amounts of energy, transforming the solid state sulfur to liquid and gas phases.

In another advantage of the present invention, heating the sulfur coated pyrite powder to 550°C results in the following decomposition reaction:



Above 440°C, S₂ gas forms around the solid pyrite particles, causing additional sulfur gas partial pressure. The additional pressure is a favorable condition for the reformation of pyrite. Consequently, the decomposition is further prevented. This is borne out by X-ray data, which show that without sulfur additive, the thin film comprises FeS, FeS_x (where x<2), Fe₂O₃, Fe₃O₄ and other undesired phases. With sulfur additive, the primary phase of the thin film (>95%) is FeS₂.

In another particularly advantageous feature of the present invention, the active material feedstock comprises nanostructured materials which, after thermal spray, results in electrodes with nanostructured active material. As used herein "nanostructured" materials refers to materials having a grain size on the order of 1 to 100 nanometers (where 1 nm = 10 angstroms). Nanostructured materials are thus characterized by having a high fraction of the material's atoms residing at grain or particle boundaries. For example, with a grain size in the five nanometer range, about one-half of the atoms in a nanocrystalline or a nanophase solid reside at grain or particle interfaces. Rapid interaction between the active materials and its surroundings are possible because of high surface area of the nanostructured materials. Therefore, the materials could sustain high current charging and discharging conditions. Thermal spray of nanostructured feedstocks to produce a nanostructured coating is disclosed in pending U.S. patent application Serial No. 09/019061, filed February 5, 1998, entitled "Nanostructured Feeds for Thermal Spray Systems, Method of

Manufacture, and Coatings Formed Therefrom," which is a continuation of U.S. patent application Serial No. 08/558,466 filed November 13, 1995, entitled "Nanostructured Feeds for Thermal Spray Systems, Method of Manufacture, and Coatings Formed Therefrom," which is incorporated herein by reference. Synthesis
5 of nanostructured materials is disclosed in application Serial No: 08/971,817 filed November 17, 1997 by Tongsan Xiao et al., entitled NANOSTRUCTURED OXIDES AND HYDROXIDES AND METHODS SYNTHESIS THEREFOR, which in incorporated herein by reference in its entirety.

Preferably, the active material feedstock, whether comprised of one of the
10 above mentioned materials or a similarly suitable material, is deposited onto a titanium or an aluminum substrate by one of the thermal spraying processes mentioned below.

Thermal spraying processes for use with the present invention are well known in the art. Known spraying processes may be classified into two groups, namely,
15 chemical combustion spraying processes and electric heating spraying processes. Chemical combustion spraying processes include powder flame spraying, wire/rod flame spraying, high velocity oxygen fuel flame spraying and detonation/explosive flame spraying. Electrical heating processes include electric-arc or twin-wire arc spraying and plasma spraying.

20

The invention is further illustrated by the following non-limiting examples.

Example 1. Electrodes Comprising Pyrite

A. Reprocessing of Pyrite

25 About 20 grams of sulfur powder is mixed with 200 grams of pyrite powder and ball milled in a ceramic jar for 24 hours. The uniformly mixed powder is then placed in a vacuum oven and dried at 150° C under vacuum for 12 hours. The surface moisture of pyrite is thereby removed and the surface of the pyrite coated by sulfur due to its low melting point (~120° C). The treated powder has much better
30 flowability, and due to high dihedral angle between sulfur and water, the treated powder was not required to be stored under a vacuum..

B. Apparatus

In general, a plasma gun is connected with a robot which has six dimension movement, and the workpiece is fixed on the sample stage. An alternative apparatus consists of a stainless steel box having a front cover accommodating a fixed plasma gun, a nitrogen gas inlet, and a robot connected to a sample holder. With this apparatus, the sample moves instead of the plasma gun, which is sealed with rubber between the front cover and the stainless steel box. With this apparatus, the oxygen content inside the chamber could be reduced to less than 5%.

The adjustable parameters of the plasma gun include arc current, argon flow rate, and carrier gas rate. If desired, the flame temperature can be decreased by reducing the arc current, and increasing the argon flow and carrier gas rates. However, an over-cooled flame will not melt the particle surfaces, resulting in a poor coating. A much preferred spray condition is achieved with 180A, and 250 SCFH argon flow.

C. Thermal Spray of Conventional (Micron and Greater-Sized) Pyrite Feedstock

Prior to thermal spray, the inert gas chamber is purged with nitrogen gas for 10 minutes. With the treated powder, coatings were produced using a Metco 9MB plasma spray system. At about 150 Ampere and 70 Volts, with 250 SCFH argon flow and 4 lb/hr feeding rate, electrodes were sprayed at conditions 3c and 5b on 1.25 inch diameter 0.006 inch thick grit blasted stainless steel disks. At both 200 and 300 Amp 250 SCFH argon conditions, the coating adhered well to the substrate, and was not fragile during handling. Also, little curling occurred indicating low stresses and the potential to spray much thicker layers.

The experiments have been carried out in the inert gas chamber with the best plasma spray conditions. The results show no evidence of iron oxide present in the deposited films. The x-ray pattern also indicates that there are more iron sulfide left in the coating compared to the one without the protection of an inert gas chamber.

Example 2. Reprocessing and Thermal Spray of Nanostructured Pyrite.

Nanostructured pyrite is synthesized by aqueous solution method at low temperature ($<90^{\circ}\text{C}$) in relatively short period (2-4 hours). Synthesized

5 nanostructured FeS_2 has particle size less than 100 nm. About 20 grams of sulfur powder was mixed with 200 gram of the nanostructured pyrite powder and ball milled in a ceramic jar for 24 hours. Thereafter, the uniformly mixed powder is placed in a vacuum oven, and dried at 150°C under vacuum for 12 hours. The treated powder then is dispersed in 10% PVA solution and the suspension is then spray dried at 200°C in accordance with U.S. Ser. No. 08/553,133 above. The particle size of reprocessed powder is in the range of 1-200 nm. The thin film electrode of pyrite was fabricated with the plasma spray by Metlco 9MB plasma gun as described above to form a nanostructure pyrite electrode.

10 Example 3. Thermal Spray of $\text{Ni}(\text{OH})_2$

The thin film electrode of $\text{Ni}(\text{OH})_2$ was fabricated with the plasma spray by Metlco 9MB plasma gun. The arc current is 120A at 70V with argon flow about 250 SCFH. The $\text{Ni}(\text{OH})_2$ powder was feed at rate of 2 lb/hr with 70 SCFH carrier gas.

Example 4. Thermal Spray of Nanostructured $\text{Ni}(\text{OH})_2$

15 Nanostructured $\text{Ni}(\text{OH})_2$ is reprocessed by spray-during the as-synthesized powders to agglomerates in accordance with U.S. Ser. No. 08/553,133 above. The thin film electrode of nanostructured $\text{Ni}(\text{OH})_2$ is fabricated by Metlco 9MB plasma gun. The arc current is 120A at 70V with argon flow about 250 SCFH. The $\text{Ni}(\text{OH})_2$ powder was feed at rate of 2 lb/hr with 70 SCFH carrier gas.

20 Example 5. Thermal Spray of MnO_2

A thin film of MnO_2 was fabricated with the plasma spray by Metlco 9MB plasma gun. The arc current is 200A at 70V with argon flow about 200 SCFH. The MnO_2 powder is a feed at rate of 3 lb/hr with 70 SCFH carrier gas.

Example 6. Thermal Spray of Nanostructure MnO_2

25 Nanostructured MnO_2 is reprocessed as in Example 3. The thin film electrode of nanostructured MnO_2 is fabricated under the same condition as Example 4.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.

5 What is claimed is:

CLAIM 1. A method for the synthesis of an electrode, comprising
coating an active material feedstock with an additive material suitable for
preventing thermal decomposition of said feedstock during thermal spray; and
thermal spraying the coated feedstock onto a substrate for an electrode,
5 thereby forming a coating on the substrate, to provide an electrode.

CLAIM 2. The method of claim 1, wherein
the electrode is a thin film electrode.

CLAIM 3. The method of claim 1, wherein
the additive material is elemental sulfur.

CLAIM 4. The method of claim 1, wherein
the additive material is cornstarch.

CLAIM 5. The method of claim 1, wherein
the substrate comprises titanium or aluminum or mixtures thereof.

CLAIM 6. The method of claim 1, wherein
the active material feedstock is a metal, a metal oxide, a mixed metal oxide, a
metal sulfide, a carbonaceous material, and mixtures thereof.

CLAIM 7. The method of claim 1, wherein
the active material feedstock is silver vanadium oxide, copper silver vanadium
oxide, manganese dioxide, copper oxide, chromium oxide, cobalt oxide, nickel
oxide, nickel hydroxide, titanium disulfide, copper sulfide, iron sulfide, iron
5 disulfide, cobalt disulfide, molybdenum disulfide, tungsten sulfide, carbon,
fluorinated carbon, and mixtures thereof.

CLAIM 8. The method of claim 1 wherein
the active material feedstock comprises pyrite.

- CLAIM 9. The method of claim 1 wherein the active material feedstock is nanostructured.
- CLAIM 10. The method of claim 9 wherein the electrode coating is nanostructured.
- CLAIM 11. The method of claim 8 wherein the active material feedstock is nanostructured.
- CLAIM 12. The method of claim 11 wherein the electrode coating is nanostructured.
- CLAIM 13. The method of claim 1, wherein the thermal spraying is carried out in an inert atmosphere.
- CLAIM 14. The method of claim 1, wherein the thermal spraying is carried out in an atmosphere comprising less than about 5% oxygen.
- CLAIM 15. The method of claim 1, wherein thermal spraying is by plasma gun.
- CLAIM 16. An electrode manufactured by the method of claim 1.
- CLAIM 17. The electrode of claim 16, wherein the electrode is a thin film electrode.
- CLAIM 18. The electrode of claim 16, wherein the additive material is elemental sulfur.

CLAIM 19. The electrode of claim 16, wherein
the additive material is cornstarch.

CLAIM 20. The electrode of claim 16, wherein
the substrate comprises titanium or aluminum or mixtures thereof.

CLAIM 21. The electrode of claim 16, wherein
the active material feedstock is a metal, a metal oxide, a mixed metal oxide, a
metal sulfide, a carbonaceous material, and mixtures thereof.

CLAIM 22. The electrode of claim 16 wherein
the active material feedstock is silver vanadium oxide, copper silver vanadium
oxide, manganese dioxide, copper oxide, chromium oxide, cobalt oxide, nickel
oxide, nickel hydroxide, titanium disulfide, copper sulfide, iron sulfide, iron
5 disulfide, cobalt disulfide, molybdenum disulfide, tungsten sulfide, carbon,
fluorinated carbon, and mixtures thereof.

CLAIM 23. The electrode of claim 16 wherein
the active material feedstock comprises pyrite.

CLAIM 24. The electrode of claim 16 wherein
the active material feedstock is nanostructured.

CLAIM 25. The electrode of claim 24 wherein
the electrode coating is nanostructured.

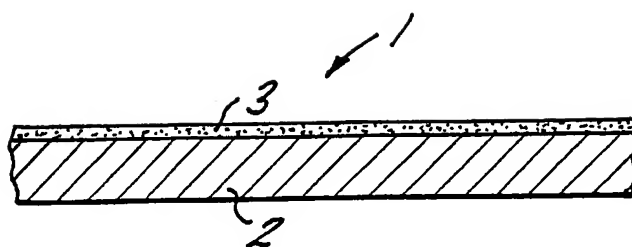
CLAIM 26. The electrode of claim 23 wherein
the active material feedstock is nanostructured.

CLAIM 27. The electrode of claim 26 wherein
the electrode coating is nanostructured.

CLAIM 28. The electrode of claim 16, wherein
the thermal spraying is carried out in an inert atmosphere.

CLAIM 29. The electrode of claim 16, wherein
the thermal spraying is carried out in an atmosphere comprising less than
about 5% oxygen.

CLAIM 30. The electrode of claim 16, wherein
thermal spraying is by plasma gun.



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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/12899

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 4/04, 4/12; H01M 4/04

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/446, 450, 453, 455, 456, 217, 215; 106/287.32; 29/623.5; 204/242

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y — A	US 5,716,422 A (MUFFOLETTO et al) 10 February 1998, see col. 2, line 44 through col. 6, line 15 and col. 10, line 35 through col. 11, line 45.	1-2, 5-17, 20-30 ----- 3-4, 18-19
Y	US 3,332,753 A (BATCHELOR et al) 25 July 1967, see col. 1, lines 20-35 and col. 2, lines 5-15.	1-2, 5-17, 20-30.
A	US 5,426,003 A (SPENGLER et al) 20 June 1995, see columns 14 and 15.	1-30

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

27 JULY 1999

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER: US CL :

427/446, 450, 453, 455, 456, 217, 215; 106/287.32; 29/623.5; 204/242

